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On the electrical resistivities of pyrolytic graphite

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A theoretical formulation of the problem of charge carrier transport in pyrolytic graphite is made and criterion defined when a relaxation time approach for scattering (in addition to normal thermal scattering), originating at the intercrystalline boundary, is justified. Taking into consideration this additional scattering the electrical resistivities (basal plane resistivity ρ_a, and c-axis resistivity ρ_c) of pyrolytic graphite are deducible from single crystal graphite transport parameters. Excellent agreement of the calculated values of resistivities with the experimental ones has been found.

Introduction

Pyrolytic graphite (PG) known for a long time has come to lime light only recently because of its application in nuclear and space technology (Bokros 1969). Its electrical properties also have many interesting features for solid state physicists (Reynolds 1968). PG is characterized by largest known anisotropy (ρ_c/ρ_a) for materials. Its (ρ_c/ρ_a) is found to have values an order of magnitude larger than that of single crystal graphite (Klein 1962) though PG in reality is made up of small single crystals of graphite (crystallites)ty pically several hundred angstroms in size in the basal plane. In PG deposited at $T_d \geqslant 2000°C$, these crystallites have a high degree of orientation with almost all the c-axes pointing along the same direction. This composite nature of PG seems to be responsible not only for the difference in its resistivity anisotropy from that of its components (crystallites) but also its dependence of resistivity on temperature. Both ρ_c and ρ_a are found experimentally to decrease with temperature like semiconductors, whereas, single crystal graphite is known to have resistivities which increase with temperature like metals.

Mrozowski (1952) attempted to explain the phenomena by assuming that in the energy band structure of PG there must be a bandgap E_g. He argued that small size of the crystallites may give rise to a bandgap instead of a band overlap as is found in single crystal graphite. But this point of view has never been elaborated in details to be generally acceptable. Several years ago Klein (1964) observed a phenomenological band overlap and an effective mass of electron somewhat different from those of single crystal graphite, which fitted only with the basal plane data for pure, highly graphitized PG.

Our approach presented here shows that electrical resistivity of PG along any direction can be deduced fairly accurately from the charge transport parameters of single crystal graphite after giving due consideration to the effect of finite size of the crystallites.

Theoretical consideration

Formulation of the Problem Let us imagine a single crystallite within the bulk of PG It is obvious that it is separated from its adjacent ones by internal surfaces all around These internal surfaces are really sites of dislocation containing carbon atoms whose σ-electrons are not bonded covalently and thus they are liable to capture mobile π-electrons from the bulk of the crystallite near the surface. Trapping of π-electrons builds a static negative charge on these surfaces, and an induced positive charge of equal amount on to the internal surface of the bulk of the crystallite, so that overall electrical charge neutrality is maintained. The surface space charge layer thus formed produces a local potential field (ϕ) which repeats in any direction j at an interval of length L_j, the crystallite's extension in that direction.

If this macroscopic potential distribution $\phi(x_j)$ were known, we could, in principle, add this to the atomic potential and solve the Schrodinger equation for wave functions ψ_j of the entire composite of crystallites with the restriction that the macroscopic potential and macroscopic charge distribution is self-consistent through Poisson's equations This seems to be the most appropriate procedure to determine the energy band structure of a composite like PG, but unfortunately $\phi(x_j)$ is not known, apart from the complexity of solving Schrodinger's wave equation when two kinds of potential functions are present.

It has been pointed out by Shockley (1950) that by the application of a small field the wave functions are not seriously distorted but change with time in a manner that can be described as a change of the wave vector K. This in effect is equivalent to a combination of effective mass approximation with the WKB methods (Schiff 1949) for the solution of the Schrödinger equation, because we have used wave functions which are dependent only on the local kinetic energy at each point. Thus, we may argue that our procedure is subject to the same limits- of validity as the WBK method *i.e*

$$\frac{d\lambda}{dx_j} << 4\pi \qquad \ldots (1)$$

where λ is the electron wavelength. Though we do not know the exact potential function $\phi(x_j)$ at the intercrystalline boundary, it is reasonable to assume that $\phi(x_j)$ will be felt over a length dx_j of the order of a Debye length (L_D). Assuming

single crystal's electron and hole concentrations, $L_D \simeq 5\text{Å}$ for graphite. So that (1) reduces to

$$d\lambda << 4\pi L_D \qquad \ldots (2)$$

or,

$$\left|\frac{dK}{K}\right| << 2|K|L_D \qquad (3)$$

Since L_D is only 5Å, $|dK/K|$ allowed for the method to be valid, is small indeed However, in case of PG, we may take the close agreement of the theoretical resistivities, calculated by considering the additional relaxation time for scattering due to the change in K at the boundary with the experimental values as a proof of the validity of the criterion (3)

Boundary Scattering Relaxation Time. With criterion (3) satisfied away from the boundary ($|x_j| >> L_D$) electron wave function ψ_K and energy $\epsilon(K)$ will be that of a single crystal In case of PG, $|x_j|$ should refer only to the two dimensions of a crystallite along the basal plane because ψ_K and $\epsilon(K)$ of a graphite crystal is mainly determined by the basal plane structure The interaction between layers through weak Van der Waal force causes only small perturbations in $\psi(K)$ and $\epsilon(K)$. Therefore, when $|L_{a,b}|$ of a crystallite is much larger than L_D, $\psi(K)$ and $\epsilon(K)$ of the crystallite may be considered identical with those of a single crystal graphite inspite of the fact that $|L_c|$ of the crystallite may be comparable to L_D. The electron in such a crystallite will therefore travel with a velocity $v_K = 1/\hbar.\nabla_K \epsilon(K)$. Assuming absence of phonon scattering (which we may take into account separately since the two processes are statistically independent), electron travelling in any direction j will be scattered, changing its wave vector from K_j to $K_j + dK_j$ in a time

$$\tau_j = \frac{L_j}{\bar{v}} \qquad (4)$$

τ_j values may be different because both L_j and v_{K_j} may have values which are not same for all x_j. However, we may in that case talk of an average crystallite size L_j and average velocity $\bar{v}_{K_j}$ and the average time for scattering to occur

$$\bar{\tau}_j = \frac{\bar{L}_j}{\bar{v}} \qquad (5)$$

For electrons and holes which take part in the conduction process, $v_{Kj} = v_{Fj}$ the Fermi-velocity. So that we may rewrite (5) as

$$\bar{\tau}_j = \frac{\bar{L}_j}{v_{Fj}} \qquad (6)$$

Now when an electric field E is applied, a force field eE operating will cause K to drift at the rate $\dot{K} = \frac{eE}{\hbar}$ When E is small, change in K in time $\bar{\tau}_j$ given by

$\Delta K = \frac{eE}{\hbar}\bar{\tau}_j$ may be considered negligibly small to effect changes in v_{Kj} and hence in $\bar{\tau}_j$ (this situation is usually met). So, under small field condition $\bar{\tau}_j$ becomes an additional relaxation time in the PG composite.

Expression for Total Resistivity. In addition to the above scattering mechanism, there is present the electron-phonon scattering as applicable to the ideal graphite crystal. Let the relaxation time for this be τ_{th}. Then we may write according to Matthiessen's rule the total resistivity in any direction j as

$$\rho_{Tj} = \rho_{Sj} + \rho_{ij} \qquad \ldots (7)$$

where the intercrystalline surface limited resistivity

$$\rho_{Sj} = \frac{1}{\frac{ne^2}{m_{ej}^*}\bar{\tau}_{ej} + \frac{pe^2}{m_{hj}^*}\bar{\tau}_{hj}} \qquad \ldots (8)$$

and the ideal graphite crystal resistivity

$$\rho_{ij} = \frac{1}{\frac{ne^2}{m_{ej}^*}\tau_{thj}^{\,e} + \frac{pe^2}{m_{hj}^*}\tau_{thj}^{\,h}}; \qquad \ldots (9)$$

n, p are the electron and hole concentrations, m_e^*, m_h^* are the effective electron and hole masses τ^e_{th} and τ^h_{th} are the electron and hole thermal relaxation times of ideal single crystal graphite. Combining equations (6) (7) (8) and (9) we obtain

$$\rho_{Tj} = \frac{1}{\frac{ne^2}{m^*_{ej}}\frac{\bar{L}_j}{v^e_{Fj}} + \frac{pe^2}{m^*_{hj}}\frac{\bar{L}_j}{v^*_{Fj}}} + \frac{1}{\frac{n^2e}{m^*_{e_j}}\tau^e_{th} + \frac{pe^2}{m^*_{h_j}}\tau^h_{th}} \qquad \ldots (10)$$

Results

Single crystal graphite transport parameters are tabulated from McClure (1958) Soule, McClure & Smith (1964), the values being accepted as the most accurate, in table 1.

Calculated values of ρ_{Ta} and ρ_{Tc} according to equation (10) and the parameters of table 1 are plotted as a function of $\bar{L_a}$ and $\bar{L_c}$ in figures 1 and 2 respectively.

For Klein's (1962) deposited sample PG R-40 crystallite size in the basal plane as determined by X-ray analysis corresponds to a value $\bar{L_a} = 285$ Å. At $L_a = 285$ Å our calculated ρ_{Ta} according to equation (10) at a temperature of 300°K is

Table 1 Single crystal graphite transport parameters

$j = a$, along basal plane. $j = c$ perpendicular to basal plane

$m^*_{ca} = 0.03 m_0$, $m^*_{ha} = 0.06\, m_0$
$m^*_{cc} = 4.39\, m_0$, $m^*_{hc} = 17.95\, m_0$ } $m_0 = 9\ 11 \times 10^{-31}$ Kgm.

	n/c	$\times 10^{18}$	cm/sec $\times 10^6$	cm/sec $\times 10^6$	sec $\times 10^{-12}$	sec $\times 10^{-12}$	cm/sec $\times 10^6$	cm/sec $\times 10^6$
4 2	2 1	2.0	0.93	0.54	10	:2	0 0768	.0312
77	2.4	2.3	0.93	0 54	0.8	2.2	0 0768	0.312
300	7.3	7.2	1.5	0.80	0 19	0.33	0 1239	.0462

0.449×10^{-3} ohm cm. Experimental value of ρ_{Ta} obtained by Klein for this sample at 300°K is $0\ 452 \times 10^{-3}$ ohm cm. Agreement between experimental and calculated values is therefore excellent. Similar agreement is found at 77°K and 4 2°K for this sample.

As a further example, we consider Klein's $R-7^*$ sample whose $\bar{L}_a$ is 700Å. Again we find agreement between the experimental value 0.21×10^{-3} ohm cm and the calculated value 0.215×10^{-3} ohm cm.

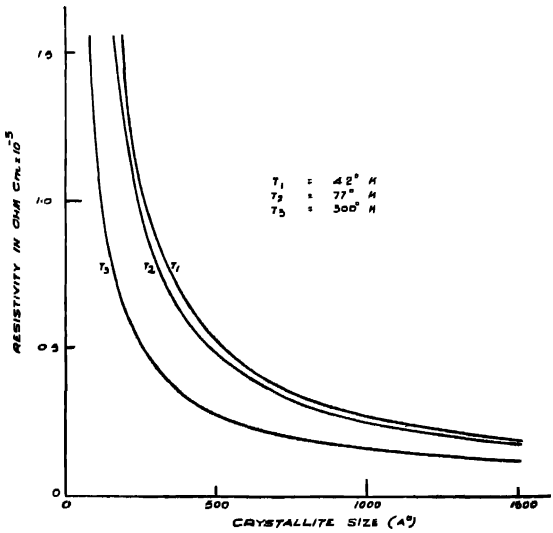

Figure 1. Theoretical basal plane resistivity of PG as a function of crystallite size along the basal plane.

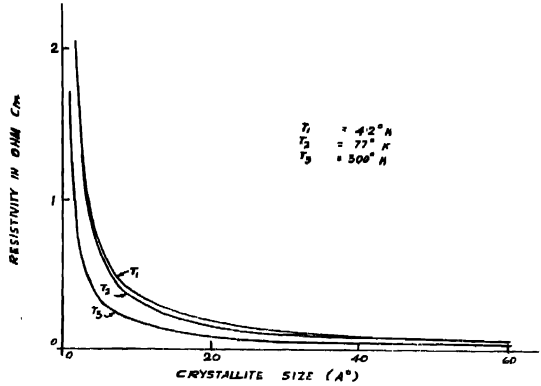

Figure 2. Theoretical c-axis resistivity of PG as a function of crystallite size along the c-axis.

In order to calculate resistivity along the c-axis, we require to know the layer spacing $\bar{L}_c$. Klein could not determine L_c by X-ray analysis because of diffused X-ray reflections. Recently $\overline{L_c}$ values were determined (Thrower 1969) and are found to have a value of $\bar{L}_c \simeq 5$Å for turbostratic graphite (deposited PG are usually turbostratic and since Klein's R-40 is a deposited sample it ought to have turbostratic structure) Putting $L_c = 5$Å in equation (10), we calculated ρ_{T_c} and obtained a value of 0.65 ohm cm at 77°K Klein's experimental value of ρ_{T_c} of R-40 sample at 77°K is also 0.65 ohm cm.

Theoretically Soule, McClure & Smith (1964) found that $\rho_c/\rho_a = 190$ at 300°K for single crystal graphite. This value of ρ_c/ρ_a is in reasonable agreement with the experimental values of Primak & Fuchs (1954). On the contrary ρ_c/ρ_a of PG as measured experimentally (Klein 1964, Saha, Banerjee & Das 1969) is found to have values ranging to several thousands. This is not surprising as can be seen from equation (10). So long $L_a << $ thermal mean free path, anisotropy of PG should increase with the ratio $\bar{L}_a/L_c$ and both ρ_{T_c} and ρ_{T_a} should decrease with increasing temperature.

Conclusion

It is shown here that a unified point of view for the origin of electrical resistivities of single crystal graphite and pyrolytic graphite is permissible so long the intercrystalline space charge layer width is much smaller than crystallites' dimensions in the basal plane. Under this condition energy band structure may be considered to remain invariant but additional scattering of charge carriers occur at the boundary. Also, the long standing confusion (Klein 1962),why PG may

have larger anisotropy in resistivity than single crystal graphite and opposite kind of temperature dependence of resistivity from that of single crystal graphite, is resolved. Besides, the concepts used in this paper may be useful in a general way for elucidating electrical properties of polycrystalline matter in terms of the parameters of its constituent crystallites.

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